Chemistry 4021/8021 **Computational Chemistry** 3/4 Credits

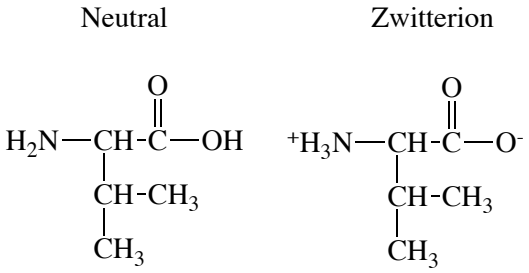
Spring Semester 2013

(Due 2 / 27 / 13)

Using PC Model, answer the questions below. If you have questions/issues working on this Problem Set, do please consider using Piazza to address them.

1. In the MMFF94 and AMBER force fields, what are the parameters for the harmonic force constants (mdyne/Å) and equilibrium bond lengths (Å) for the bond between an alkyl carbon and an ammonium group as might be found in, say, $H_3C—NH_3^+$? How closely do the two sets of constants agree? Discuss the significance of any difference.

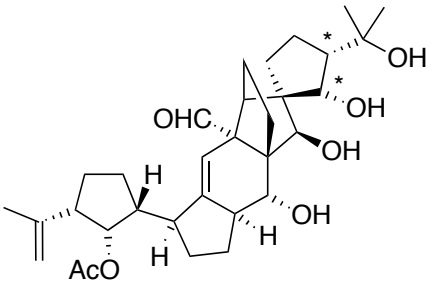
   Optimize all of the torsional conformers of the zwitterionic form of the amino acid valine using the MMFF94 force field. What are the relative energies for the conformers? Now compute the analogous conformers for the neutral form of valine. Discuss your results and include a description of any additional steps you had to take to make this comparison. (Nota bene: pay close attention to your atom types throughout.) Although you are not asked to do it here, to increase confidence in your results, what could you do?



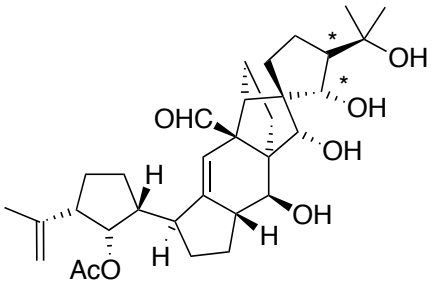
Valine

2. One of the two structures below is that originally assigned to a certain natural product. The other is the correct structure, determined later through (extremely costly) total synthesis. Use GMMX and the MM3 force field to find the lowest energy conformations for both structures **A** and **B** (use the default energy window for saving structures). In addition, monitor the coupling constant between the protons on the vicinal centers marked by asterisks. Report the 298 K Boltzmann average coupling constant for both structures. Under what

circumstances would you be able to use the computed coupling constant to distinguish between the two possible structures? Note that if you are not confident about interpreting the stereochemistry implied by the drawing for any of the 13 stereogenic centers (or anything else!) please ask.



A



B

Send Josh a copy of your ____2.pcm file for each structure by email so that he can verify your structures.

3. Find a paper in the chemical literature published since from 2008–2013 that includes a molecular mechanics calculation that you can reproduce in PC Model (you don't have to reproduce it *exactly*, but you should be able to at least follow the same line of inquiry; thus, for instance, the paper might use a force field not found in PC Model, but for a molecule for which *other* force fields in PC Model might be expected to be perfectly fine). Turn in a copy of the original paper and a brief description of what you did and how your calculations compared to those in the paper. Rationalize any differences in results. If you have doubts or concerns along the way, sound off on Piazza or talk to any of the instructors.